

Scientists Are Using the Unique Capabilities of the Protein Crystallography Station at LANSCE to Understand Electrical Anomalies in α -Glycine

Glycine, the smallest of the amino acids, functions as a neurotransmitter and is one of the principle components of structural proteins, enzymes, and hormones. Glycine exhibits complex chemical behavior, crystallizing into three polymorphic zwitterionic (neutral) crystal structures (α , β , and γ) and converting to its nonionic form when vaporized. Depending on pH levels, glycine can adopt a cationic (positive charge), zwitterionic, and anionic (negative charge) form. A structural understanding of the mechanism behind an electrical anomaly observed in single crystals of glycine at the atomic level could lead to the identification and design of new materials with enhanced electrical properties.

Past measurements of the electrical conductance (the ability to conduct electrical charge) and capacitance (the ability to store electrical charge) of a single crystal of α -glycine revealed anomalous electrical properties that were dependent on temperature [T.C. Chilcott *et al.*, *Philosophical Magazine B* **79**, 1695-1901 (1999)]. Cooling the crystal from 50°C slowly decreased its electrical conductance until it reached 31°C. Further cooling caused a dramatic increase in the crystal's conductance! A similar anomaly occurred in the electrical capacitance of the crystal — capacitance is essentially temperature independent above 31°C but decreases precipitously below this temperature. The usual mechanisms used to explain insulating single crystals could not adequately describe these observations. Instead, it was suggested that perhaps a phase transition of the α -glycine crystal causes a pyroelectric occurrence — the property of certain crystals to produce a state of electrical polarity by a change in temperature.

In 2001, researchers from Los Alamos National Laboratory in collaboration with the Institut Laue Langevin (ILL) carried out a variable-temperature neutron-diffraction study of α -glycine at the high-flux nuclear reactor run by the ILL [P. Langan *et al.*, *Acta Crystallographica B* **58**, 728-733 (2002)]. Neutron diffraction was used instead of the standard technique for determining crystal structures, x-ray diffraction, because it can provide more accurate information on hydrogen atom positions. Hydrogen atoms are expected to play an important role in the phenomenon under investigation. The results from the analyses of six complete data sets collected over a temperature range of 288 K to 427 K proved that pyroelectricity could not explain the anomalous electrical properties observed in the single-crystal samples. In these experiments, the unit cell expanded anisotropically with increasing temperature. The unique b axis, which corresponds to the stacking direction of molecular layers, showed the most change. The increasing separation of anti-ferroelectric molecular layers with increasing temperature is driven by oscillations about the axis perpendicular to the b axis (Fig. 1). The interlayer hydrogen bonds also weakened with temperature, but there was little evidence of any change in the polarization of the bonds.

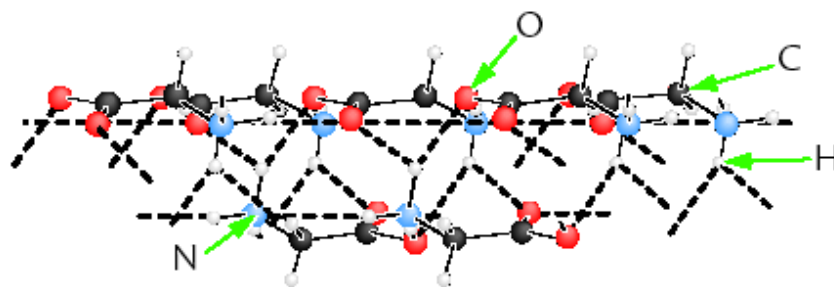


Fig. 1. A view perpendicular to the b axis of α -glycine showing a hydrogen-bonded anti-parallel double layer. The bifurcated hydrogen bonds between single layers are represented by dashed lines.

Although the results of the experiment at the ILL dismissed the possibility of pyroelectricity or a phase transition as the cause of the anomalous electrical behavior, they did suggest another possible mechanism. Glycine molecules in their zwitterionic form have a large associate electric dipole moment. The increasing separation of the molecular layers would change the ability of these dipoles to reorient in an applied electric field and therefore change the electrical properties of the crystal. To investigate this possibility, scientists from the Bioscience Division are carrying out new experiments on the Protein Crystallography Station (PCS) at LANSCE (Fig. 2). These experiments are the *first ever* neutron-diffraction studies of electric-field-induced structural changes in an organic single crystal. As such, they hope to directly determine the reorientation of the molecular dipoles in the applied electric field and how this reorientation relates not only to the observed increase in oscillation of the axis that is perpendicular to the b axis but also to the separation of molecular layers. They would also like to determine whether the molecular reorientation has significant effects on the interlayer hydrogen bonding and therefore the hydrogen-bond and molecular polarizations as well.



Fig. 2. Paul Langan of Biosciences Division points out the single-crystal sample (shown in the inset) of α -glycine used in the current experiments on the PCS.

The PCS is an ideal instrument on which to carry out this type of experiment because of the combination of neutron time-of-flight techniques with a large-area detector (Fig. 2). On a conventional neutron diffractometer, both the crystal sample and the detector are moved so that diffraction data can be collected reflection by reflection. On the PCS, however, all data are collected at the same time without moving the crystal or detector. Data can therefore be collected in a parametric fashion as a function of temperature or electric field, and very subtle changes can be detected in the diffraction data.

In preliminary measurements, a clear change in the diffraction data of α -glycine has been observed at ambient temperature when an electric field of 100 mV is applied across the crystal. The data are currently being analyzed to relate these changes to changes in crystal structure.

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